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ORIGINAL ARTICLE

1,4,7,10-Tetraazacyclododecane incorporating salicylic acid moieties synthesis and properties

Anna Skwierawska · Ewa Paluszkiewicz · Monika Przyborowska · Tadeusz Ossowski

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Abstract The synthesis of salicylic acid derivatives of 1,4,7,10-tetraazacyclododecane has been described. The complexing properties of these compounds towards metal cations were investigated by absorption and emission spectroscopy, and ^{1}H NMR. The X-ray structure of **L-2** nitrate is reported.

Keywords Cyclen · Salicylic acid · Complexes · X-ray structure

Introduction

1,4,7,10-Tetraazacyclododecane derivatives have demonstrated a broad spectrum of uses, including chemistry, pharmaceuticals, medicine, and environmental protection [1–4]. Conceptually the simplest and most convergent method of preparation mono and disubstituted ligands is direct alkylation or acylation of cyclen [5–8]. Although one-pot procedure is simple, the three-step procedure in which protected 1,4,7,10-tetraazacyclododecane is prepared first, followed by alkylation or acylation reaction followed by deprotection, has generally been found to result in higher yields [9–11].

We are particularly interested in direct synthesis of hydroxy acid derivatives of 1,4,7,10-tetraazacyclododecane. Hydroxy acids and their derivatives are known as efficient chelating reagents for metal cations. For example, salicylic acid forms complexes with Al^{+3}, Fe^{+3}, Cu^{+2}, Co^{+2}, Mg^{+2} and Ca^{+2} [12]. Introduction of hydroxy acid moieties to macrocycle should efficiently modify complexing ability of entire molecule. So far three 1,4,7,10-tetraazacyclododecane derivatives containing salicylic acid residue were synthesized (Fig. 1) [13, 14]. Compounds **1**, **2** and **3** have light-harvesting moieties but only ligand **1** exhibits moderate fluorescence. UV–Vis Spectroscopic studies show that compound **1** forms complexes only with Co^{2+} ions while both compounds **2** and **3** are able to complex Mg^{+2}, Ca^{+2}, and Sr^{+2} cations. The obtained results suggest that the structure of substituent (salicylic acid derivative) is crucial for selective cation recognition. In this paper we present synthesis and spectroscopic studies of new salicylic acid derivatives of cyclen.

A. Skwierawska (✉) · E. Paluszkiewicz
Chemistry Department, Gdańsk University of Technology, Narutowicza St. 11/12, 80-952 Gdansk, Poland
e-mail: skwieraw@chem.pg.gda.pl

M. Przyborowska · T. Ossowski
Chemical Department, Gdańsk University, Sobieskiego St. 18, 80-952 Gdansk, Poland

Experimental

General

^{1}H NMR and ^{13}C NMR spectra were recorded at 500 MHz and 125 MHz on Varian instrument, respectively. Mass spectra were recorded using a VG Platform II electrospray mass spectrometer with methanol as a carrier solvent. Elemental analysis was performed on Carlo Erba CHNS-O EA 1108 apparatus. UV spectra and fluorescence emission spectra were recorded on a Perkin Elmer Lambda 40P spectrophotometer and a Perkin Elmer LS-50B fluorescence spectrophotometer, respectively.

Thin layer chromatography (TLC) analyses were carried out on Alufolien covered with silica gel 60-F-254 (0.2 mm thickness) while silica gel 60 (70–230 mesh) was used for column chromatography.

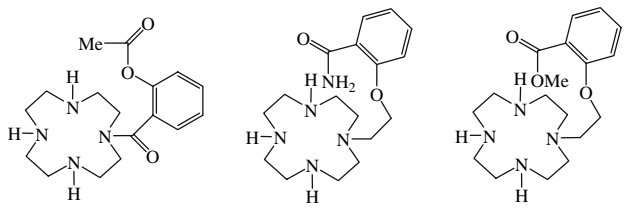


Fig. 1 Synthesized salicylic acid derivatives of 1,4,7,10-tetraazacyclododecane

All reagents and solvents were of the highest commercial quality and were used without further purification. $Zn(ClO_4)_2 \cdot 6H_2O$, $Cu(ClO_4)_2 \cdot 6H_2O$, $Co(ClO_4)_2 \cdot 6H_2O$, $Ni(ClO_4)_2 \cdot 6H_2O$, $Cd(ClO_4)_2 \cdot 6H_2O$, $Al(ClO_4)_3 \cdot 9H_2O$ and $Al(NO_3)_3 \cdot 9H_2O$ were purchased from Aldrich. All salts were dried under vacuum at 60 °C before use. Acetonitrile was dried over calcium hydride before use. Water refers to high purity water with conductivity of ≤ 0.03 μS cm^{-1}, obtained from the HYDROLAB purification system. 1,4,7,10-Tetraazacyclododecane (Strem Co., France), salicylic acid and 4-nitrophenol (Aldrich) are commercially available and were used as received.

Potentiometric titrations were performed in water at 25 °C using an OP-205 Radelkis pH-meter linked to a personal computer. All the test solutions (50 mL) were kept under argon (>99.999% purity) atmosphere. The potentiometric pH titrations were carried out with $I = 0.1$ ($NaNO_3$) at 25.0 ± 0.1 °C, and at least two independent titrations were performed. Protonation constants were determined by means of the STOICHIO program [15].

UV–Vis spectra and fluorescence emission spectra were recorded at 25.0 ± 0.1 °C on a Perkin Elmer Lambda 40P spectrophotometer and a Perkin Elmer LS-50B fluorescence spectrophotometer, respectively. For fluorescence titration, a sample solution was excited at 310 nm or 294 nm if **L-1** was studied, and 288 nm or 283 nm if **L-2** was used. The obtained data from UV titrations were analyzed for apparent complexation constants K using the STOICHIO program [15].

1-N-Salicyloyl-1,4,7,10-tetraazacyclododecane (**L-1**) and 1,7-bis-*N,N′*-salicyloyl-1,4,7,10-tetraazacyclododecane (**L-2**)

A stoichiometric amount of 4-nitrophenyl active ester [16] (5 mmol, 1.3 g) was added to a solution of cyclen (5 mmol, 0.9 g) in dry THF (15 mL). The reaction mixture was stirred for 10–12 h at room temperature. The solvent was evaporated under vacuum, and the oily residue was purified by gradient column chromatography, using solvent system $CHCl_3$/MeOH/NH_3. Fraction, which was eluted with 40:1:0.1 ($CHCl_3$:MeOH:NH_3) mixture was collected giving **L-2** (0.3 g, 20%, $R_f = 0.25$) as a colorless oil after solvent evaporation. Further increasing of solvent polarity up to 20:4:1 ($CHCl_3$:MeOH:NH_3) allowed separation of **L-1** (0.9 g, 60%, $R_f = 0.19$), as a colorless oil.

L-1: ^{1}H NMR (d-DMSO): 2.48–2.49 (m, 2H), 2.54–2.55 (m, 2H), 2.63–2.64 (m, 2H), 2.69–2.71 (m, 2H), 2.79–2.82 (m, 4H), 3.47–3.48 (m, 4H), 5.20–5.40 (br, 4H), 6.45 (t, $J = 7.3$ Hz, 1H), 6.55 (d, $J = 8.3$ Hz, 1H), 6.97 (dd, $J = 1.5$ and 7.8 Hz, 1H,), 7.02 (dt, $J = 1.5$ and 7.3 Hz, 1H); ^{13}C NMR: 44.34, 45.86, 46.74, 47.58, 47.70, 48.32, 49.20, 51.82, 114.97, 119.70, 126.02, 129.76, 130.81, 159.57, 172.96; HRMS [EI, (M^+)] calculated for $C_{15}H_{24}N_4O_2$ 292.18993; found 292.19035; Anal. Calcd. for: $C_{15}H_{24}N_4O_2$: C, 61.62; H, 8.27; N, 19.16. Found: C, 61.56; H, 8.30; N, 19.13.

L-2: ^{1}H NMR (d-DMSO): 2.66–2.67 (m, 5H), 2.89–2.93 (m, 5H), 3.34–3.44 (m, 8H), 6.66 (t, $J = 7.3$ Hz, 2H), 6.70–6.72 (m, 2H), 7.05 (d, $J = 7.3$ Hz, 2H), 7.11–7.12 (m, 2H) 8.01 (s, 2H); ^{13}C NMR: 45.26, 46.97, 48.07, 48.68, 50.01, 117.22, 118.22, 125.91, 128.51, 130.26, 156.24, 171.60; HRMS [EI, (M^+)] calculated for $C_{22}H_{28}N_4O_4$ 412.21106; found 412.21196; Anal. Calcd. for: $C_{22}H_{28}N_4O_4$: C, 64.06; H, 6.84; N, 13.58. Found: C, 64.01; H, 6.86; N, 13.56.

[**L-2**] · 2 (HNO_3) · CH_3CN preparations

1,7-Bis-*N,N′*-salicyloyl-1,4,7,10-tetraazacyclododecane (0.1 mmol, 41 mg) was dissolved in acetonitrile (10 mL) and $Al(NO_3)_3 \cdot 9H_2O$ was added. The mixture was refluxed 2 h then left at the room temperature for several days. Single crystals were collected, washed with acetonitrile and dried.

Anal. Calcd. for: $C_{22}H_{28}N_4O_4 \cdot 2(HNO_3) \cdot CH_3CN$: C, 49.74; H, 5.74; N, 16.92. Found: C, 49.70; H, 5.80; N, 16.89. M.p. 160 °C (decomposition).

X-ray structure description

1,7-Bis-*N,N′*-salicyloyl-1,4,7,10-tetraazacyclododecane nitrate single crystal was grown as result of alumina nitrate hydrolysis in acetonitile during complex preparation. For X-ray studies a transparent crystal of needle shape was selected. X-ray measurements were carried out on a KUMA KM4 four-axis diffractometer equipped with a Sapphire-2 CCD detector (Oxford Diffraction) at working temperature 120 K (Oxford Cryosystem).

Data collection: CrysAlis CCD (Oxford Diffraction [17], 2005); cell refinement: CrysAlis RED (Oxford Diffraction, 2005); data reduction: CrysAlis RED; program(s) used to solve structure: SHELXS97 (Sheldrick [18], 1997); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: ORTEP-3 for Windows [19]

(Farrugia, 1997); software used to prepare material for publication [20]: WinGX (Farrugia, 1999). All H atoms were positioned geometrically (C–H = 0.95–0.99 Å) and refined as riding with their U_{iso} values constrained to be x times U_{eq} of their pivot atom (x = 1.2 for aromatic C–H, 1.3 for methylene C–H and 1.5 for methyl C–H). The N–H and O–H bonds were constrained to 0.92 Å. The highest electron density peak (0.24) is located 0.86 Å from atom C1.

Crystallographic data for the structure reported in this paper has been deposited with the Cambridge Crystallographic Data Centre as Supplementary Publication No CCDC 634437.

Copies of the data can be obtained free of charge from the CCDC (12 Union Road, Cambridge CB2 1EZ, UK; Tel.:+44-1223-336-408; fax:+44-1223-336-003; e-mail: deposit@ccdc.cam.ac.uk; http://www.ccdc.cam.ac.uk).

Results and discussion

The reaction of salicylic acid chloride with 1,4,7,10-tetraazacyclododecane afforded a mixture of products. The yield of the monosubstituted product after column separation was only 10%. The use of 1,4,7-tri-*tert*-butoxycarbonyl-tetraazacyclododecane allowed to obtain the product after deprotection and column purification with the yield of 15%. In this situation another method was attempted. Among available acylation reagents of salicylic acid, active esters were chosen. Thus, 4-nitrophenyl active ester of salicylic acid was prepared in reaction of salicylic acid and 4-nitrophenol using $POCl_3$ as condensing agent in toluene solution [16]. In the next step, the active ester was used in the substitution reaction (Scheme 1).

Cyclen (1 mmol) and the active ester (1 mmol) were dissolved in dry THF. The solution was left for 10–12 h at room temperature. The progress of acylation was controlled by TLC. In the reaction only mono- and disubstituted products were formed, although the reagents were used in molar ratio 1:1 and high dilution condition was not applied. The yield of monosubstituted product (**L-1**) was 60%. It is worth to note that changes of reaction conditions such as elevated temperature 40 °C and 1:2 molar ratio (cyclen: active ester) allowed to obtain diamide as the major product (**L-2**) with 60% yield.

L-2 forms crystals at presence of nitrate anions in acetonitrile solution. We obtained single crystals of **L-2** nitrate as results of hydrolysis reaction of $Al(NO_3)_3$ during complex preparation. X-ray study reveals that in the crystal structure of **L-2** the asymmetric unit contains half of the cyclen molecule sitting at the symmetry center (Wyckoff position [21] *f*), one nitrate anion and one molecule of acetonitrile in general positions. Elemental cell is composed of one macrocyclic dication, two NO_3^- ions and two molecules of CH_3CN. The macrocyclic molecule carries double positive charge due to protonation of both N2 and N2′ atoms. Figure 2 shows described above structure and extra nitrate anion for better illustration of hydrogen bonds.

Both N–H are involved in hydrogen bonding. One is intramolecular: H2a uses O2 phenolic oxygen as the acceptor, whereas H2b forms intermolecular bond with oxygen atom O4′ from the nitrate anion. Hydrogen atom (H2c) from the phenolic O–H group forms a different intermolecular bond to another oxygen atom O3″ of the anion (Table 1). The solvent (CH_3CN) is not involved into hydrogen bonding and simply fills space in cavities of the crystal structure.

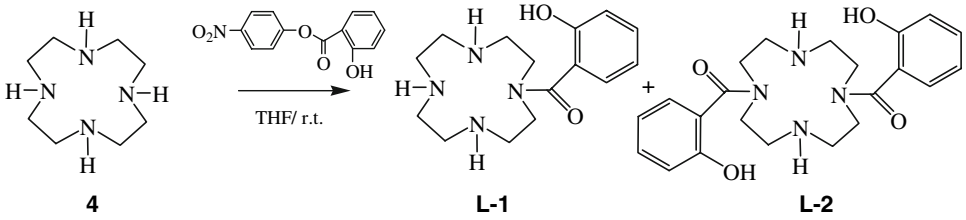
The protonation constants (K_n) of **L-1** and **L-2** were determined by potentiometric and spectrophotometric pH titrations of the acidic solutions of **L-1** ($C_{L\text{-}1} = 4.72 \times 10^{-4}$ M, $C_{H+} = 1.17 \times 10^{-3}$ M CH_3SO_3H) and **L-2** ($C_{L\text{-}2} = 3.03 \times 10^{-4}$ M, $C_{H+} = 8.54 \times 10^{-4}$ M CH_3SO_3H) against 1.83×10^{-2} NaOH (**L-1**) and 8.94×10^{-3} M NaOH (**L-2**) with $I = 0.1$ ($NaNO_3$) at 25 °C. The titration data were analyzed for the acid-base equilibrium 1 and 2, where a_{H+} is the activity of H^+.

$$K_1 = [L]/[H_{-1}L]a_{H+}$$
$$K_n = [H_{n-1}L]/[H_{n-2}L]a_{H+}$$
$$(n = 2, 3, 4)$$

The protonation constants K_n were calculated and were collected in Table 2 as pKa.

Figure 3 showed pH dependent UV titrations of ligands **L-1** and **L-2** ($\lambda = 300$ nm). The increase of absorbance was observed in both cases, but the shape of the curves was different. If compound **L-1** was used, absorbance increase was observed in pH range 3.5–7 while the absorbance value of **L-2** was almost constant. In the pH range 7–11 the increase of absorbance was observed for both ligands, but

Scheme 1 Direct acylation of cyclen with 4-nitrophenyl salicylate



4 L-1 L-2

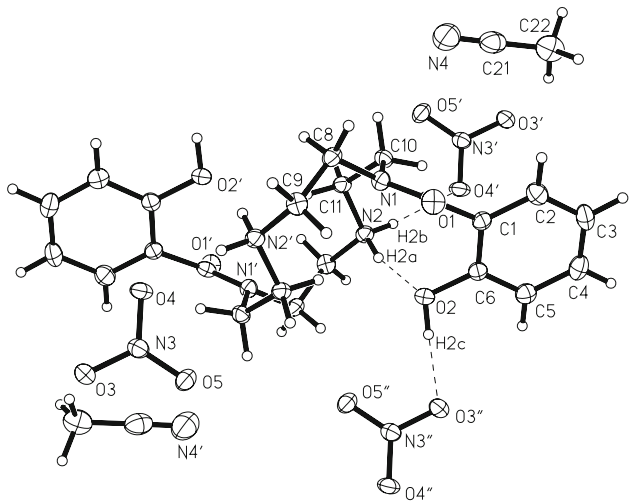


Fig. 2 ORTEP plot of **L-2**, showing the atom labeling scheme. Displacement ellipsoids are drawn at 50% probability level. Symmetry transformations used to generate equivalent atoms: primed: $-x + 1, -y, -z + 1$ doubly primed: $-x + 2, -y, -z + 1$. One more NO_3^- anion (equivalent) is shown to reveal hydrogen bonding connectivity

Table 1 Hydrogen bonds for **L-2** [Å and °]

D–H···A	d(D–H)	d(H···A)	d(D···A)	<(DHA)
N(2)–H(2a)···O(2)	0.92	1.94	2.838(3)	165.5
N(2)–H(2b)···O(4′)	0.92	1.99	2.871(3)	159.7
O(2)–H(2c)···O(3″)	0.92(4)	1.75(4)	2.655(3)	167(3)

the absorption intensity of **L-2** increased about 35% compared to **L-1** of pH 10.

Complexing properties of **L-1** and **L-2** with metal cations were studied first in acetonitrile solution. In case of Zn^{2+} ions several equilibriums of very strong complexes were found for both ligands and the calculation of complexation constants was impossible. To simplify the system, acetonitrile was replaced by water. In aqueous solution **L-1** (absorption maximum at 300 nm, $\varepsilon = 1860$ $[M^{-1} \cdot cm^{-1}]$) formed also several complexes with Zn^{2+}cations. The spectroscopic UV–Vis titration is shown in Fig. 4a. The increase of the absorbance band at $\lambda = 281$ nm and decrease of the band at $\lambda = 300$ was observed. The course of titration of **L-2** (absorption maximum at 300 nm, $\varepsilon = 3650$ $[M^{-1} \cdot cm^{-1}]$) was comparable to **L-1** but, in the contrast, **L-2** formed only one ionic complex $[Zn(\mathbf{L\text{-}1})_2]^{2+}$ for which log β value was estimated as 8.44 ± 0.09 (Fig. 4b).

Compound **L-2** formed also complexes with Cd^{2+} and Al^{3+} cations (Fig. 5a, b). The stoichiometry of complex with Cd^{2+} was 1:1 and the value of log K was estimated to be 4.34 ± 0.05. In case of spectroscopic titration of **L-2** with $Al(ClO_4)_3$ the formation of new band at $\lambda = 340$ nm was observed and two types of equilibrium in methanol solution was found. The stoichiometry of complexes were 1:1 and 1:2 (Al^{3+}: **L-2**), but the main form was the second one.

Complex formation has also been studied by ^1H NMR. The main problems in these experiments were: strong influence of different solvents and poor solubility of

Table 2 Protonation constants of **L-1** and **L-2** of the acidic solutions of ligands against NaOH with $I = 0.1$ ($NaNO_3$) at 25 °C calculated by STOICHIO program [14]

p*K*a	p*K*a	p*K*a	p*K*a	p*K*a	p*K*a	p*K*a
Potentiometric pH titrations of the acidic solutions of compounds **L-1** and **L-2**						
10.52 ± 0.06	8.29 ± 0.03	5.94 ± 0.03	2.20 ± 0.34	10.68 ± 0.23	9.09 ± 0.03	7.63 ± 0.02
Spectrophotometric pH titrations of the acidic solutions of compounds **L-1** and **L-2** at 300 nm						
–	8.18 ± 0.01	5.96 ± 0.02	–	10.26 ± 0.01	9.04 ± 0.11	–

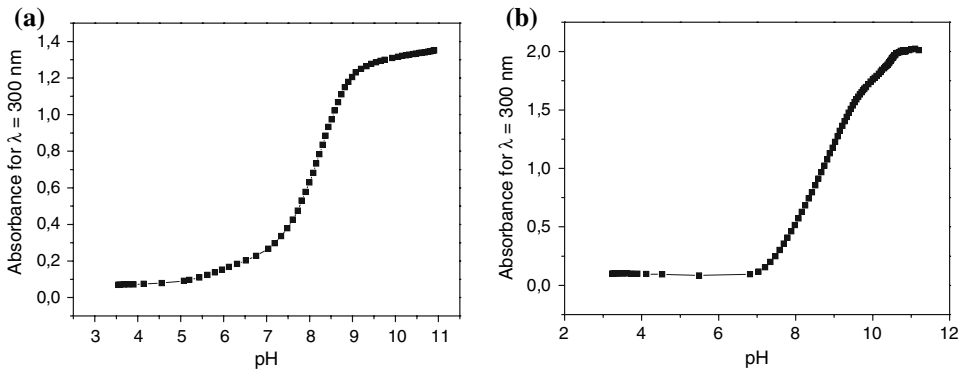


Fig. 3 (**a**) pH Depended UV-pH for **L-1** ($C_{\mathbf{L\text{-}1}} = 4.72 \cdot 10^{-4}$ M, $C_{H+} = 1.169 \times 10^{-3}$ M, $C_{NaOH} = 8.943 \times 10^{-3}$ M) at 25 °C with $I = 0.1$ ($NaNO_3$); (**b**) UV-pH profile for **L-2** ($C_{\mathbf{L\text{-}2}} = 3.03 \times 10^{-4}$ M, $C_{H+} = 8.54 \times 10^{-4}$ M, $C_{NaOH} = 1.083 \times 10^{-2}$ M) at 25 °C with $I = 0.1$ ($NaNO_3$). The experimental points are open squares and the fitting curve for the model is a line

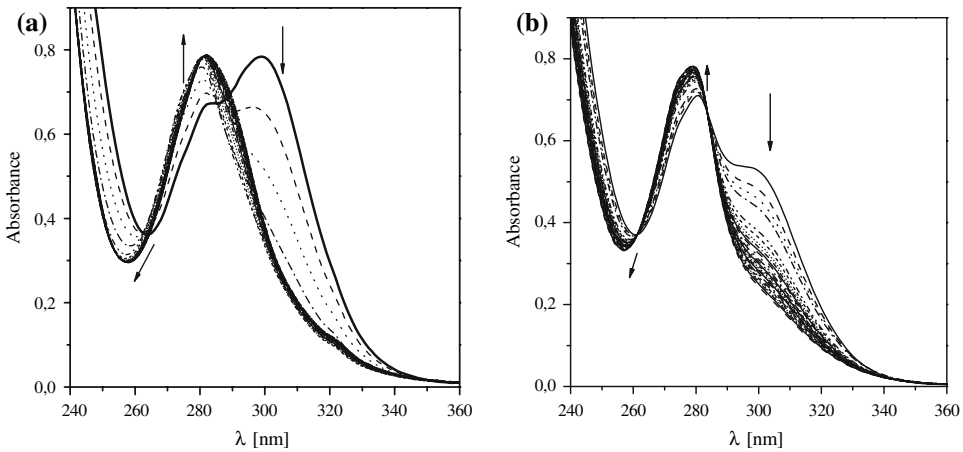


Fig. 4 (**a**) Absorption spectra recorded in water solution containing ligand **L-1** (4.24×10^{-4} M) with $Zn(ClO_4)_2$ (0–2.27×10^{-3} M). (**b**) Absorption spectra recorded in water solution containing ligand **L-2** (1.95×10^{-4} M) with zinc perchlorate (0–1.24×10^{-3} M)

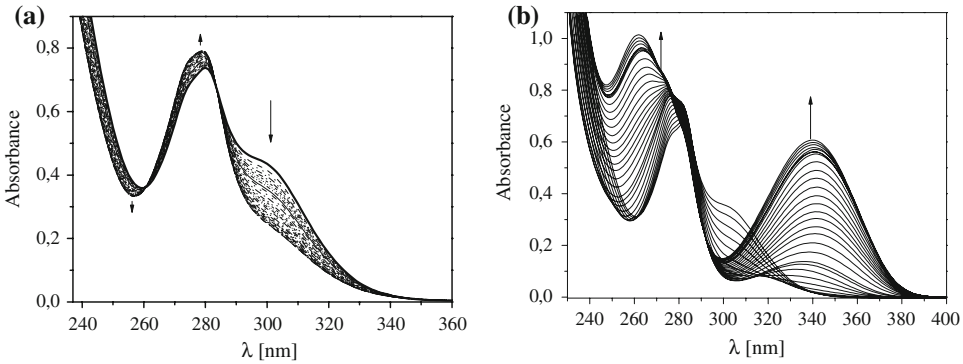


Fig. 5 (**a**) Absorption spectra recorded in water solution containing ligand **L-2** (2.02×10^{-4} M) with $Cd(ClO_4)_2$ (0–1.43×10^{-3} M). (**b**) Absorption spectra recorded in methanol solution containing ligand **L-2** ($c = 1.68 \times 10^{-4}$ M) with $Al(ClO_4)_3$ ($c = 0$–8.32×10^{-4} M)

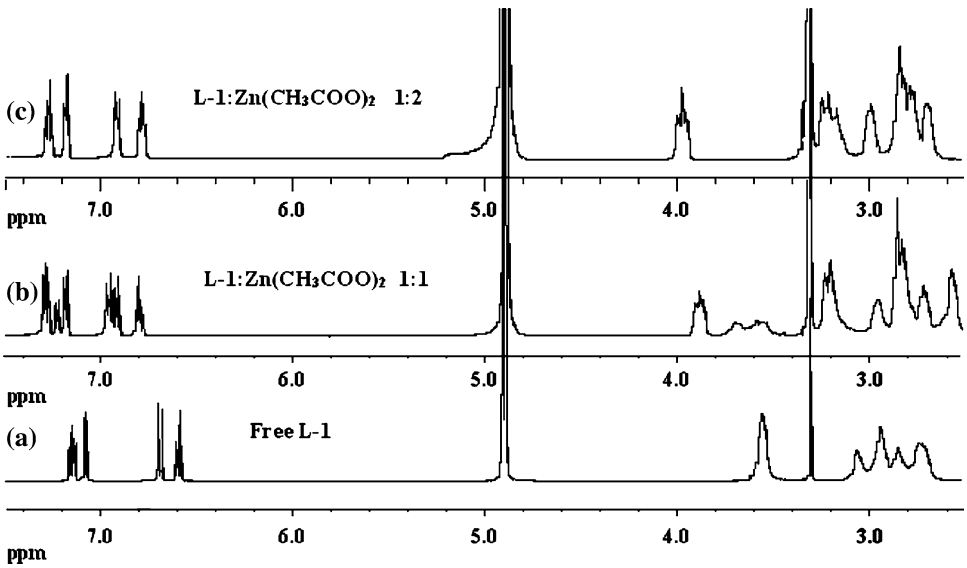


Fig. 6 ^{1}H NMR spectra of ligand **L-1** recorded in d-methanol: (**a**) free ligand **L-1**; (**b**) equilibrium between free ligand **L-1** and complexes; (**c**) complex of **L-1** with zinc acetate

complexes in the majority of used solvents. The simplest spectra of free ligands were obtained in d-methanol, but the solubility of **L-2** complexes in pure d-methanol was insufficient and finally a mixture of d-methanol and d-chloroform was used.

In the spectrum of free **L-1** five broad signals at 2.5–3.6 ppm and four well defined signals at 6.7–7.3 ppm were observed (Fig. 6a). Addition of zinc acetate caused gradual increase of complex signals and diminution of host signals (Fig. 6b). Moreover, in the solution which contains **L-1**

and zinc acetate in molar ratio 1:2 only complex signals can be recorded (Fig. 6c). However, it was difficult to judge which of nitrogen atom was engaged in complex formation. The observed changes of spectra in the aliphatic region could suggest that at least two of nitrogen atoms were involved in complex formation.

The spectra of free ligand **L-2** and its complexes with zinc acetate were recorded in the mixture of d-methanol and d-chloroform (7:1.5 v/v) (Fig. 7).

Firstly, salt addition caused broadening of all peaks. Formation of the new signals became when 2:1 (**L-2**:Zn $(CH_3COO)_2$) ratio is achieved. Afterwards increase of intensity of complex signals was observed. The most complex spectra were those recorded during complex formation of **L-2** with aluminum nitrate. The results are shown in Fig. 8. Gradual salt addition caused significant changes especially in aliphatic region. That might suggest formation of several complexes in solution.

Fluorescent responses of **L-1** and **L-2** to various metal ions in acetonitrile solution (excitation at 310 nm for **L-1** and 288 nm for **L-2**) were studied. The emission of **L-1** was more or less quenched by Ni^{2+}, Co^{2+}, Cu^{2+} and Cd^{2+}. On the other hand, Zn^{2+} enhanced the emission and shifted the emission band. Fluorescence titrations of **L-1** were performed for selected cations (Fig. 9). In case of titration of **L-1** (7.14×10^{-5} M, $\lambda_{exc} = 294$ nm) with Cd^{2+}, cations gradual

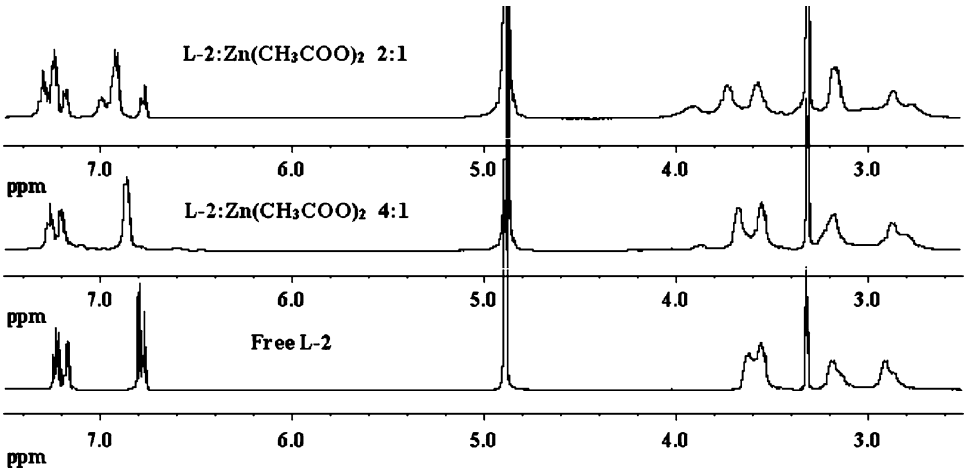


Fig. 7 ^{1}H NMR spectra of free ligand **L-2** and its complex with zinc acetate recorded in the mixture of d-methanol and d-chloroform

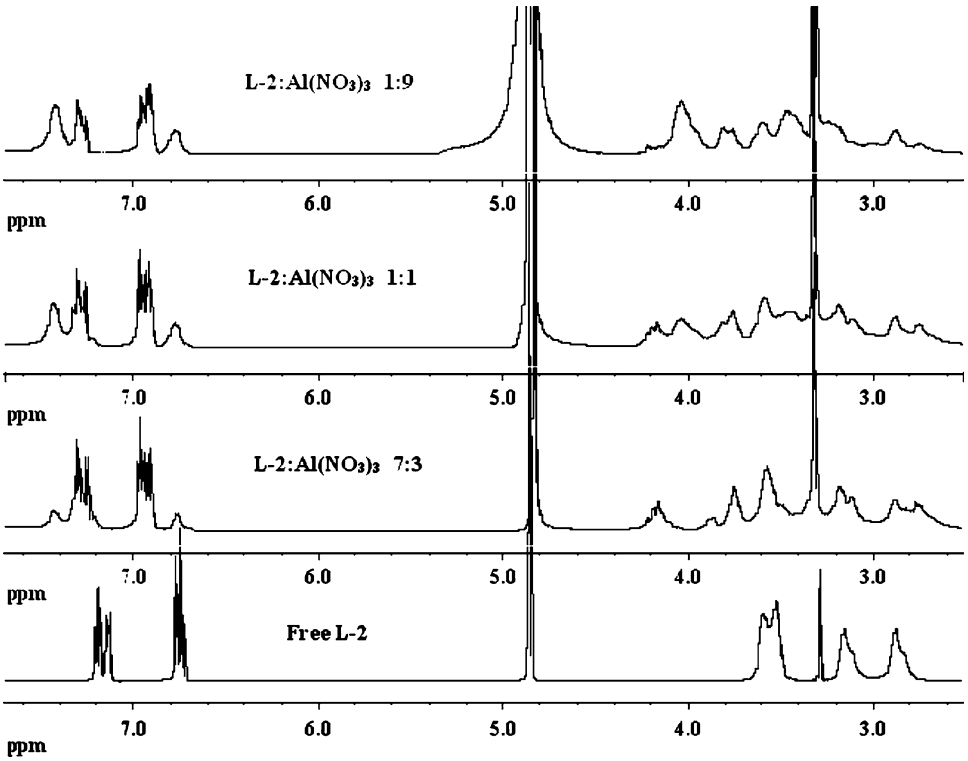


Fig. 8 ^{1}H NMR spectra of free ligand **L-2** and its complex with aluminum nitrate recorded in the mixture of d-methanol and d-chloroform

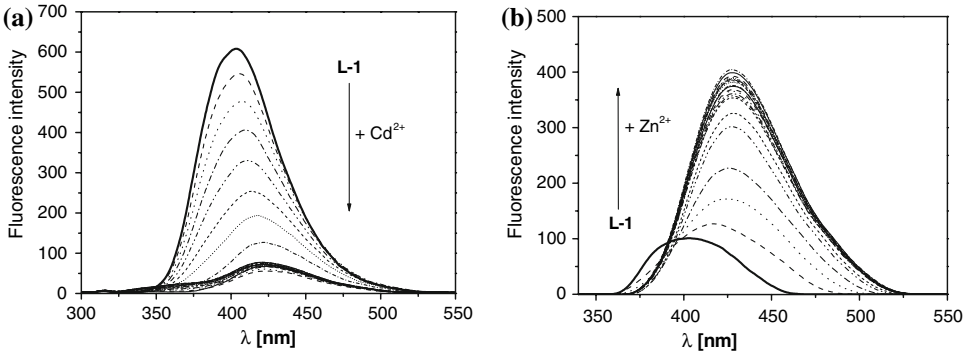


Fig. 9 Emission spectra recorded in acetonitrile solution containing: (**a**) ligand **L-1** (7.14×10^{-5} M) with cadmium perchlorate (0–3.84×10^{-4} M), (**b**) ligand **L-1** (6.63×10^{-5} M) with zinc perchlorate (0–4.76×10^{-4} M)

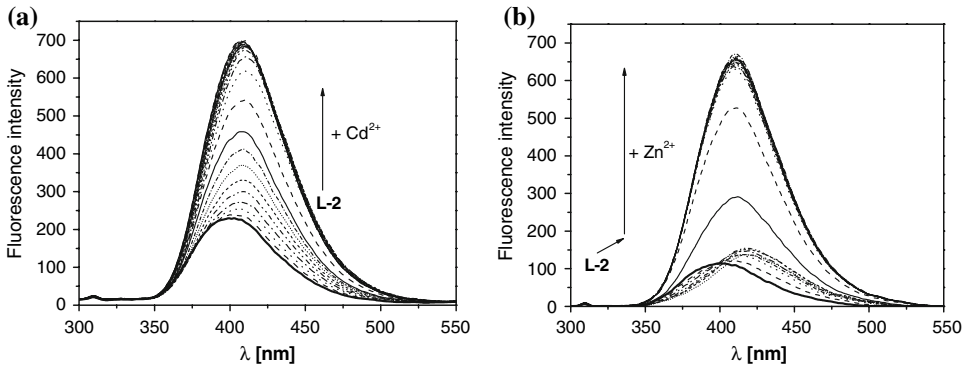


Fig. 10 Emission spectra recorded in acetonitrile solution containing ligand **L-2** (2.52×10^{-5} M, $\lambda_{exc} = 283$ nm) with (**a**) cadmium perchlorate (0–1.39×10^{-4} M), (**b**) zinc perchlorate (0–1.42×10^{-4} M)

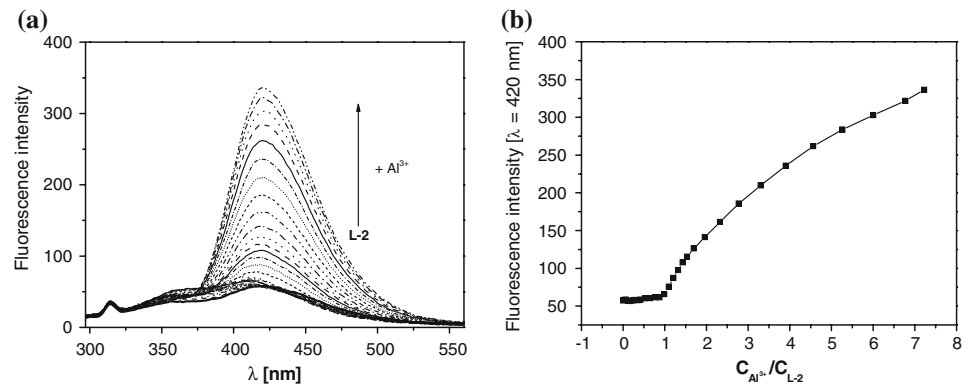


Fig. 11 Emission spectra recorded in methanol solution containing (**a**) ligand **L-2** (2.57×10^{-5} M) with aluminium perchlorate (0–1.86×10^{-4} M), (**b**) Dependence of fluorescence intensity at 420 nm for ligand **L-2** with aluminium perchlorate

decreasing of emission band was observed (Fig. 9a). After addition of 8.4×10^{-9} mol of $Cd(ClO_4)_2$ the emission decreased 10 times. Further titration caused only insignificant changes. Similar results were obtained for other cations, but the addition of just 1×10^{-6} mol of Zn^{2+}effected in increasing emission (**L-1** 6.63×10^{-5} M). After addition of the 2×10^{-6} mol the emission rose 4 times (Fig. 9b).

Compound **L-2** showed different properties. Among studied cations Cd^{2+} and Zn^{2+} increased the emission, while Co^{2+}, Ni^{2+} and Cu^{2+} completely quenched the emission. Fluorescence titrations of **L-2** with Cd^{2+} and Zn^{2+} are shown in Fig. 10. In case of titration with Cd^{2+}, the gradual increase of the emission band was observed. After addition of 5×10^{-7} mol of $Cd(ClO_4)_2$ the emission increased 2.5 times. In the case of Zn^{2+} the characteristic band shift and slow increase of emission was observed up to the addition of a 3×10^{-7} mol of $Zn(ClO_4)_2$. Increased Zn^{2+} additions caused significant changes and greatly enhanced the emission (6 times).

Furthermore **L-2** showed significant emission enhanced by the presence of Al^{3+}. The major emission enhancement was observed after the addition of 1 equivalent of Al^{3+} (Fig. 11). Plot of emission versus Al^{3+}: **L-2** ratio showed an insignificant increase of the emission band up to molar ratio 1:1 (Al^{+3}: **L-2**), then a great enhancement in the emission at $\lambda = 420$ nm took place. Complexation with Al^{+3} ions increased tenfold the emission intensity at 420 nm (Fig. 11b).

Conclusions

The alternative, very selective reaction of monoacylation of unprotected cyclen has been described. The possibility to use the same synthetic pathway for diamide preparation was mentioned. UV–vis and pH titration allowed us to determinate p*K*a values for both compounds. The obtained results from two different methods were comparable.

L-1 selectively binds zinc cations. The introduction of the second amide group to cyclen considerably changes complexing ability of **L-2**. Compound **L-2** forms complexes with Zn^{2+}, Cd^{2+}, and Al^{3+} cations. Newly designed amide cyclen derivatives with one or two fluorescing salicylic acid moieties provide novel properties to salicylic fluorescence by itself and by metal complexes. The addition of Ni^{2+}, Co^{2+}, and Cu^{2+} perchlorates caused quenching of the emission bands of presented ligands, but in contrast to **L-1**, compound **L-2** forms fluorescent complexes not only upon addition of Zn^{2+}, but also Cd^{2+} and Al^{3+}. The presence of free hydroxyl group strongly influences fluorescence and complexing ability of molecules.

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